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The SUN system was ordered in September 1986. After long delays in production, the system was partially delivered in January-February 1987. The system was installed within two weeks and became functional in April-May 1987. Due to reduced amount of funds granted ($150,000) a supplementary fund was obtained from the National Science Foundation ($30,000) and Clarkson University has contributed $20,000 as well, With these combined funds the system was made functional, after an ethernet installation.

Several achievements can already be reported by the use of the SUN system despite its short service time.

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greatly enhanced. For example, this document is prepared on the SUN system. (2) Our University installed a link to the NYSERNET; and our Ethernet was connected to it. As such, we have the ability to logon our supercomputer accounts from the SUN system, that is to say that we do the development of programs on the SUN's. If much time is required, we logon a supercomputer, transfer the files and run. The SUN allows us to have interactive ability with the various supercomputers around the U.S.A. (3) Communications. We have a flexibility of routing communications via the various links associated with the NYSERNET. In particular, when a link has some down time and communication is needed instantly, the SUN is the only way we can establish E mail and electronic communications.

B. Scientific. Various scientific projects were accelerated as well as new ones started due to the arrival of the SUN system. A typical paper is enclosed. It has been typed on the SUN and most of the numerical results were obtained by using the SUN system.

Two project summaries are enclosed as well: 1) Studies on Optical and X-Ray Resist Processes (by Dr. E. Matijevic and Dr. E. Barouch); and 2) Theoretical and Experimental Investigation of the Interaction of Unlike Particles (by Dr. E. Barouch and Dr. S.V. Babu)

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A copy of the original purchase order is enclosed.

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B. Scientific

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Two project summaries are enclosed as well. One summarizes the achievements with Professor Matijević and the PI, the other with Professor Babu and the PI. It is anticipated that several other projects will be completed soon by other PI's as well.

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Studies on optical and x — ray resist processes

Fabrication of VLSI devices has made enormous strides over the last

several years, helped by technological advances at all levels of processing of

such devices. Pattern dimensions continue to shrink with improvements in

materials and manufacturing yields. At the same time the United States

is falling behind in several key processing technologies in this area and is

steadily loosing market share as international competition continues un-

abated. This proposal is aimed at strengthening the knowledge base and

enhancing the availability of trained man-power in this country in the area

of sub-micron lithography – an area that is vital to all VLSI device pro-

cessing.

Typically circuit patterns, designed by the device engineer, are trans-

ferred onto the semiconductor substrate by lithographic processes in several

steps. A latent image is formed in a polymeric resist material by exposing

it to optical, e-beam, x-ray, etc. radiation through a mask. The image is

chemically developed to produce a three dimensional relief structure. The

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developed pattern is then transferred to the underlying substrate by, for example, etching with the residual resist acting as an in situ mask. Shrinking pattern dimensions, now in the sub-micron domain, and higher circuit densities demand faithful replication of the design pattern with little or no tolerance for error.

New operating environments and resist materials are continually being proposed to enhance the resolution capabilities of the microlithographic process. The limiting resolution of the currently available lithographic tools and resist materials has been estimated to be in the range of 0.5–0.7 μ m. X-ray lithography can potentially lower this limit to 100–200 nm, but is currently utilized mainly in the laboratory. Present pace of developments, particularly by the Japanese companies, suggests that its viability as a manufacturing process is just around the corner. In any case, technological advances have outstripped process modeling in all lithographic applications. The potential resolution capabilities are far from being achieved in a manufacturing environment, limited by an incomplete understanding of the complex interplay between the exposure and development variables on one hand, and their impact on the resist performance on the other. In

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fact, Neureuther and Oldham write in a recent review that "It is difficult to answer even the simplest question, such as what developer concentration and prebake temperature are optimum", and that there is a "widening gap between materials and quantitative models .....". Consequently, process optimization, frequently caried out empirically under manufacturing conditions, remains expensive and time consuming. Thus there is a compelling need for continuing the study of microlithographic resist processes and obtain new insights that will benefit the process engineer.

Substantial progress has, of course, been achieved over the last decade in simulating the performance of positive photoresist materials. The pioneering papers of Dill, Neureuther, and their collaborators, and more recently the work of Mack, led to the formulation of the simulation programs SAMPLE and PROLITH. To a great extent current understanding of positive photoresist performance is based on the results of these computations. In the absence of experimental data, the simulation predictions are widely used for testing approximate models.

The prediction of developed image profiles has been typically performed by utilizing the aerial image intensity distribution as an initial condition

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in an approximate iterative solution of the nonlinear coupled partial differential equations that are used to model the photoresist exposure-bleaching and development processes. However, several analytical approaches to characterize the performance of diazo-type positive photoresists have also been investigated with success, and offer the possibility for achieving new insights. This proposal is intended to enhance and extend these approaches, and to fully realise their technological benefits.

The exact results obtained by the PI for the diazo-type positive photoresists are described in the next section, followed by a discussion of their usefulness to the semiconductor industry. Extension of these results to x-ray lithography, in view of its mounting importance to the next generation of devices, is imperative.

Summary of results obtained by the PI

A. Matched Substrates:

As a first step, the pair of coupled nonlinear partial differential equations describing the exposure-bleaching process in a diazo-type positive photoresist have been solved exactly, in the absence of substrate reflectivity. The

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exact solution is given in closed form by

$$z = \int_{e^{-I_o C t}}^{M} dy \{ y\left[A(1-y) - B\ell ny\right]\}^{-1} \tag{1}$$

Here M is the concentration of the photoactive compound (PAC) at any lateral position x, and depth z into the resist film, for any exposure dose $D(x,t) = I_o(x,t)t$, with t being the exposure time. A,B,C are the usual resist parameteres, with the difference that A and B are non-dimensionlized by multiplication with the resist thickness. In the case of projection, proximity, or contact exposure through a mask, $D(x,t)$ is determined by the appropriate aerial image intensity $I_o(x,t)$. Then numerical evaluation of the integral in equation (1) for various values of the upper limit M, for the given $D(x,t)$, will fix the depth z into the resist film where M is the concentration of the PAC. Thus equation (1) allows complete determination of $M(z,x,t)$ for diazo-type resists for any exposure optics, using only quadratures. $I(z,x,t)$ is then determined by direct substitution.

$$I = I_o \frac{[A(1-M) - B\ell nM]}{\{A(1 - e^{-I_o Ct}) + BCI_o t\}} \tag{2}$$

Equation (1) has several other interesting properties. In particular, the partial derivatives of M with respect to t (or x) and z are proportional to

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each other. This proportionality of the two derivatives, on substitution into the recently derived exact integral expression for the contrast, yields the following explicit analytical expression for the contrast.

$$\gamma = +\ell n(10)CD \left[\frac{R_b}{R_t} - 1\right] \left\{A\left[1 - e^{-CD}\right] + BCD\right\}^{-1} \qquad (3)$$

Equation (3) has universal validity and is not dependent on the specific functional form of the resist dissolution rate in the developer. The resist dissolution rate only at the top and bottom of the film $-R_t$ and R_b, respectively – the exposure dose, and the usual A,B,C parameters, are required to evaluate this expression for the contrast.

Some of the recently proposed resist materials, like polysilanes, bleach nonlinearly in contrast to the linear diazo-type resists. These inorganic polysilanes have been used by Harrah and Zeigler of Sandia Laboratories for direct image formation on exposure. IBM researchers have also used these polysilanes, in combination with diazo-type resists, in bi-layer contrast enhanced lithography (CEL), following the work of Griffing and West of General Electric based on a different class of materials. The CEL process is potentially capable of generating nearly vertical side walls in the latent

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image even in the sub-micrometer domain. However, due to the presence of two layers of resist materials, a penalty of an increased exposure dose has to be paid. The exact results given by equations 1 and 2 above have been incorporated into the simulation program SAMPLE to speed up convergence when applied to the CEL process.

The system of equations describing the CEL process is similar to that for a single layer diazo-type photoresist exposure, except that the simultaneous exposure bleaching of both the layers must be described. This system of equations have also been solved exactly in a closed form, again in the absence of substrate reflectivity, and utilized to investigate the minimization of the dose penalty as well as the evolution of the image profiles.

B. Reflecting substrates

All the incident photon flux is not absorbed by the resist film and a part of it reaches the substrate and is reflected back. The underlying substrate topography is generally uneven, further enhancing its reflectivity. Interference between the incoming light wave and the reflected wave sets up a standing wave pattern in the photon intensity in the resist film lead-

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ing to a loss in lithographic resolution. Furthermore, researchers at Sandia Laboratories have discovered that even the diffuse reflectivity from the substrate degrades the resist performance significantly. Several proposals have been made to minimize the substrate reflectivity, with as yet no universally agreed optimal process.

Consequently, analysis of the lithographic process must include the effects of standing waves. The PI obtained the electric and magnetic fields in an absorbing thin film in the presence of standing waves. The resulting expressions for the optical intensity and the PAC concentration are being numerically evaluated presently.

C. Variational formulation for the dissolution trajectories

The latent image formed in the resist by the exposure process is developed using aqueous alkaline solvents. The exposed resist is preferentially dissolved in the developer solvent at a rate that depends primarily on the concentration of the PAC. The unexposed resist has the PAC left intact, and hence has a negligible dissolution rate. For a fixed dissolution time, the progress of the resist development process can be visualized as the march-

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ing forward with development time of a set of trajectories, each connecting an initial point on the surface of the resist with a unique terminal point inside the resist. The location of the terminal point depends, for fixed process conditions, only on the development time. As the development time increases, the trajectory marches inward into the resist. The locus of the terminal points reached by all the trajectories for a given development time is the final contour of the lithographic image.

For a given pair of points on any continuous trajectory, the development time required for the solvent penetration is unique and, in fact, a minimum. Based on this observation it has been possible to determine the shape of the lithographic image from the solution of a partial differential equation obtained from a variational formulation.

FUTURE WORK

The exact results obtained so far have proven to be valuable to the lithographic community. As described earlier, optimization of the CEL process is a powerful example. More aplications are currently under way.

Nevertheless, full realization of the potential of this approach requires

further research into several problems.

1). Exposure to multiple wavelengths:

The set of partial differential equations used to model the resist exposure-bleaching process is valid only for resist exposure with monochromatic radiation. In practice, a set of diserete wavelengths are utilized for the resist exposure.

2). An ultimate goal in photoresist modelling is an accurate prediction of the line profiles over any substrate topography. A major computational feature in the simulation of resist profiles is the introduction of the string algorithm by both SAMPLE and PROLITH for the dissolution process. In its use a certain amount of arbitratiness, however, is unavoidable. In particular, the decision of adding and subtracting points along the moving front is at the discretion of the user. Furthermore, the justification for this operation is not physically clear. In this priposal, we introduce a new idea, that encompasses the string algorithm spirit. Physically, we impose the least action principle. Specifically, it requires that the development path will be the path of least resistence to developer penetration. Consequently,

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minimum dissolution time is required for the development of the final line profile. As usual, this idea manifests itself in a variational calculation of the path integral along the development trajectory. This trajectory is obtained uniquely as a solution of a second order ordinary differential equation whose boundary conditions are the initial and final points of the trajectory, and its coefficients are expressed in terms of the development-rate function. The differential equation is solved numerically using a standard Runge-Kutta routine for initial value problems and finite element scheme for boundary value problems. In either a variable step size is used to optimize computation time. The PAC concentration is obtained from the corresponding Dill's equations for the exposure-bleaching process. The procedure has been implemented and tested first on a simpler process, i.e. one with no standing waves. It has been found to be very accurate and a sufficiently fine mesh eliminates the path crossings inherent in the predictions of the string algorithm. Thus the arbitrary elimination of unfavorable points is avoided.

Using our solution of standing waves [1] within the resist, we plan to implement the variational principle for reflecting substrates and multi-level

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resists. Preliminary results look very promising. Once the implementation of the standing waves problem is complete, a comparison of SAMPLE, PROLITH, and the new variational calculation with experimental results will be provided.

It should be noted that once the concentration of the resist and the development function are obtained, the least action principle is equally valid for all geometries, thus providing us with a general method to predict the line profiles for various resist topographies.

It is anticipated that the variational calculation will enhance our ability to predict line profiles accurately.

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Introduction

The primary objective of this program is to investigate theoretically and experimentally the interactions of unlike particles. This problem is considerably more involved than the interactions of identical dispersed matter, yet it is of paramount interest in order to understand more realistic systems found in nature and many applications. It is readily recognized that most materials one encounters consist of more than one kind of particles. One need only to think of soils, blood, smoke, and polluted rivers, etc. or diverse industrial products such as pigments, paper-pulp, catalysts, and ceramic powders in order to comprehend the significance of such studies.

In view of the complexity of the problems involved, the experimental approach requires models sufficiently well defined, so that the results can be used to test the underlying theories. On the other hand, the variety of interactions and geometries of interest require appropriate theoretical models that can be efficiently tested.

In view of the above comments, an interdisciplinary effort for solving these problems seems essential. Several years ago a cooperative program dealing with composite systems was launched by Professors E. Matijević (Department of Chemistry) whose specialties include preparation and properties of colloid dispersions and E. Barouch (Department of Mathematics) whose specialties include the theory of particle interactions, as well as cooperative phenomena. This program is being supported by the NSF AFOSR and heavily dependent on theSUN system.

Accomplishments

In order to gain some answers to the imposed problems, we are in the

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process of carrying out extensive experimental and theoretical studies.

Theoretical Studies

Interactions of unlike particles have been evaluated by considering two spheres that differ in composition, size, and surface potential, immersed in an electrolytic medium of varying ionic strength. This problem has been outstanding for a long time, and various approximations were introduced. While these attempts were partially successful, some rather unrealistic results were obtained as well.

A new study has been launched by the PIs, in which the problem was addressed by a detailed analysis of the two-dimensional Poisson- Boltzmann equation in its full nonlinear form. The electrostatic interaction displayed a counterintuitive effect; namely, partial attraction develops between particles of like sign potentials but unequal in magnitude. Furthermore, at very short separations, one obtains a net attraction. This result explains the common occurance, not previously understood, that two such particles can attract each other and stick together, although they bear the same sign of surface potential. It provided <u>lower</u> than previously anticipated potential profiles, yielding considerably more realistic interaction energies. The potential profiles so obtained were applied to various experimental studies

.

(a) Detachment

The Kramers diffusion equation was analyzed and solved exactly for a plate-sphere system. A surprising result was obtained. At the beginning of the detachment process, there is a large deviation from a first order kinetic reaction. Recently the analysis included the short range but powerful

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Born-wall repulsion, thus providing an improved estimate of the activation energy, essential to detachment and peptization processes. Again, unexpected results have been found, such as that with increasing ionic strength, the rate of adhered particles should increase, as indeed experimentally documented.

(b) Heterocoagulation

The potential curves were used in a detailed analysis of stability parameters, and the results provided an agreement between theory and experiments. In particular, we may now predict the conditions which control selective coagulation, as well as heterocoagulation of the same system, as demonstrated on the pigment-fluorocarbon latex system.

Service to the Scientific Community.

The interest in the results of our studies is best documented by the large number of requests for computatons of interaction energies based on our theory. These requests came from academic institutions, government laboratories, and industry.

Computations have been carried out at the request of Professors Gilbert and Napper of the University of Sydney, Australia, which have been used in their most recent publications, on the formation of polymer latex .

Another set of computations were carried out for Dr. M. Visca, Montedison, Italy for the mixed pigment-latex system, which is the subject of another accepted paper.

One more example of such service is the set of calculations we preformed for Professor Usui of Tohoku University, Sendai, Japan for his systems of

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bubble-flotations.

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CALCULATION OF IMAGE PROFILES FOR CONTRAST ENHANCED LITHOGRAPHY +

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ABSTRACT

Simultaneous bleaching of a contrast enhancing film (CEF) and the underlying positive photoresist is considered in the absence of any interface or substrate reflectivity. The intensity transmitted by the CEF is determined as a function of exposure time exactly using the absorptivity of the film in Dill's Model equations. Corresponding to this time dependent transmitted intensity, the concentration profiles in the positive photoresist have been expressed exactly in closed form. Relations, that implicitly define the developed image profile, are derived assuming that the resist development can be approximated by a two stage process. Furthermore, they are solved numerically for a polysilane – AZ2400 resist system and a model CEM-388-Resist combination proposed by Mack. The predicted image profiles are in excellent agreement with the experimentally determined profiles of Hofer et al., for the polysilanes, and the predictions of PROLITH for the model system of Mack.

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In contrast enhanced lithography (CEL) [1], [2] a conventional UV resist is coated with a thin bleachable contrast enhancing film (CEF) that exhibits "bleaching latency" [3]. Exposure of the CEF above a certain threshold level results in increased transmission, while exposures below the threshold produce little change. Significant improvement in the quality of projection printed features has been reported by Griffing and West for 0.5μm images [1]-[2], and by Hofer et al., [3], for 1.0μm images using CEL. Griffing and West [1], [2] used an undisclosed organic dye for the CEF, while Hofer et al., [3] used a 0.2μm thick aliphatic polysilane as the CEF. Hofer et al., also reported that the nonlinear bleaching of the polysilane film used by them was well described by an effective concentration dependent Dill's "A" parameter [4], given by

$$A_{eff} = [0.5 + 1.4(M_c - 0.4)]A \qquad (1)$$

where M_c is the concentration of the unbleached polysilane, with absorbance A.

Recently Dill's model equations for the exposure – bleaching of "linear" resist materials have been solved exactly in the absence of standing waves [5], and the solution extended to the image reversal process with positive photoresist [6]. More recently, Dill's model equations have also been solved in a closed form when the bleaching characteristics are nonlinear [7]. It has been applied to the simultaneous bleaching of a positive resist and that of a contrast enhancing polysilane film, assuming that the reflections can be ignored. As Oldham argues [8] ignoring reflections "is actually appropriate in many cases since the CEL itself is a major aid in suppressing reflections". In any case, the effects of reflections from the interfaces can be included

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using the recently derived closed form solution for the optical absorbtance of thin films in the presence of standing waves [9]. A comprehensive discussion of all reflections and standing waves in the CEL process will be presented in a later publication.

In this paper, using the closed form solution for the concentration of the photoactive compount (PAC) in the underlying photoresist film, an implicit functional relation for the developed image contour is derived. The derivation assumes, following Greeneich [10] and Watts [11], that resist dissolution proceeds down to the substrate in the z-direction first, followed by a lateral development in the x-direction [12]. The final image profile is obtained for an AZ-2400 resist film exposed through a polysilane layer and developed in an AZ-2401 developer. The calculated images are in excellent agreement with the images reported by Hofer et al., [3]. Developed image profiles have also been calculated for the model CEL-positive resist combination investigated by Mack [13] using PROLITH to simulate CEM-388. The two calculations are in good agreement.

Bleaching of the CEF

First, the intensity transmitted by the CEF is determined as a function of position and time. The simultaneous bleaching of the underlying photoresist is determined as a function of position and exposure using this transmitted intensity.

Equation (1) may be rewritten more generally as

$$A_{eff} = \alpha M_c + \beta \qquad (2)$$

with the subscript c denoting the CEF and where α and β are two material

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dependent constants. For the CEM class of materials proposed by Griffing and West [1] and investigated by Mack [13], α in equation (2) is equal to zero.

The bleaching of the CEF is described in terms of Dill's model equations by

$$\frac{\partial M_c}{\partial t} = -I_c M_c C_c \tag{3}$$

and

$$\frac{\partial I_c}{\partial z} = -(\alpha M_c^2 + \beta M_c + B_c) I_c. \tag{4}$$

with the initial and boundary conditions

$$M_c(z, x, 0) = 1 \quad 0 \leq z \leq 1 \tag{5}$$

and

$$I_c(0, x, t) = I_0(x) \quad \text{for all } x \text{ and } t. \tag{6}$$

Here z is the normalized depth into the CEF measured from the top, x is a lateral co-ordinate measured across the image and used to define the incident aerial image intensity $I_0(x)$, B_c is the exposure independent absorption parameter [4], C_c is the bleaching rate, and t is the exposure time.

Following Babu and Barouch [5], a first integral for M_c can be written as

$$\frac{\alpha}{2} M_c^2 + \beta M_c + B_c \ell n M_c + \frac{\partial}{\partial z} \ell n M_c = f(z) \tag{7}$$

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where $f(z)$ is an integration constant. Substitution of $t = 0$ and use of (5) in (7) yields $f(z) = \alpha/2 + \beta$. Then (7) can be integrated as

$$z = \int_{g(x,t)}^{M_c(z,x,t)} d\ell ny \{\frac{\alpha}{2}(1 - y^2) + \beta(1 - y) - B_c \ell ny\}^{-1}. \qquad (8)$$

The lower limit $g(x,t)$ is yet to be determined. It is obtained as $M_c(0, x, t)$ upon substituting $z = 0$ in (8). But from (3) and (6),

$$g(x) = M_c(0, x, t) = exp[-I_0(x)C_c t]. \qquad (9)$$

Differentiating (8) with respect to t, and combining it with (2), one also obtains

$$I_c(z, x, t) = \frac{I_0(x)[\frac{\alpha}{2}(1 - M_c^2) + \beta(1 - M_c) - B_c ln M_c]}{\frac{\alpha}{2}[1 - e^{-2I_0(x)C_c t}] + \beta[1 - e^{-I_0(x)C_c t}] + B_c I_0(x)C_c t} \qquad (10)$$

The ratio $I_c(1, x, t)/I_0(x)$ is a measure of the improvement in the contrast of the aerial image due to the nonlinear bleaching of the CEF.

Bleaching of the Positive Resist

Simultaneously, as the transmission of the CEF increases, bleaching of the photoactive compound (PAC) in the underlying positive resist continues. The bleaching of the PAC is described by

$$\frac{\partial M}{\partial t} = -IMC \qquad (11)$$

and

$$\frac{\partial I}{\partial \delta} = -(AM + B)I \quad 0 \leq \delta \leq 1. \qquad (12)$$

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with A,B,C being the usual resist parameters and M the concentration of the PAC. A and B, as well as the depth parameter δ, are nondimensionalized using the photoresist thickness. Thus, $\delta = 0$ at the CEF-resist interface and $\delta = 1$ at the resist – substrate interface.

The initial condition is still given by

$$M(\delta, x, 0) = 1 \tag{13}$$

but the boundary condition for $I(\delta, x, t)$ at $\delta = 0$ is now time dependent due to the increased transmission of the CEF.

$$I(0, x, t) = I_c(1, x, t) \tag{14}$$

and is determined from equation (10).

However, this does not create any difficulty for solving (11) and (12). Again following Babu and Barouch [5], the solution $M(\delta, x, t)$ is determined implicitly in the absence of substrate reflectivity, as

$$\delta = \int_{h(x,t)}^{M(\delta,x,t)} d\ell n y \{A(1 - y) - B\ell n y\}^{-1}. \tag{15}$$

The lower limit $h(x, t)$ is determined, as before, by substituting $\delta = 0$ in (15) and then using (14) in (11),

$$h(x, t) = M(\delta = 0, x, t) = exp[-C \int_0^t I_c(1, x, t)dt]. \tag{16}$$

This completes the determination of the closed form solution of the PAC concentration profile in the CEL process, when interface reflectivities are not significant.

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CEL Image Profile Calculation.

The resist dissolution process can be approximately represented by a two-stage process [10], [11]. In the first stage, dissolution proceeds in the z-direction till all the resist is cleared from the substrate in the regions of maxima in the transmitted intensity. This is followed by dissolution in the lateral (x) direction till the end of the development process.

Let the total development time be t_d, and the phenomenological dissolution – development rate function be given by R[M] (see reference [13], [14]). Then

$$t_d = t_\delta + t_x \qquad (17)$$

where

$$t_\delta = \int_0^{\delta(x)} \frac{d\delta'}{R[M(\delta', x)]} \qquad (18)$$

t_δ is determined by setting $\delta(x) = 1$ for all x where $I_c(1, x, t)$ has a maximum. At other values of $x, \delta(x)$ is fixed using this value of t_δ in (18).

Changing the variable of integraton from δ to M in (18) and replacing $(\partial\delta/\partial M)_x$ with the result obtained by differentiating (15), one obtains

$$t_\delta = \int_{M(0,x,t)}^{M(\delta,x,t)} \frac{dM}{M[A(1 - M) - B\ell nM]R(M)} \qquad (19)$$

or

$$t_\delta \equiv f(M_b, M_t). \qquad (20)$$

The dependence of the integral in (19) on the exposure process is now only through the limits of integration, which are determined implicitly by

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(15). The subscripts b and t in (20) denote the bottom ($\delta = 1$) and top ($\delta = 0$) of the photoresist layer.

Then

$$t_x = t_d - t_\delta = \int_{x_i(\delta)}^{x_f(\delta)} \frac{dx}{R[M(\delta, x)]}. \tag{21}$$

Here $x_i(\delta)$ is the line profile calculated after a development time of t_δ and is determined from (18). The final developed image profile, given by $x_f(\delta)$, has to be determined by solving (21) for the given t_d and the t_δ obtained from (18). t_x can also be rewritten in terms of the function f of (20) by changing the variable of integration to M and recognizing that

$$\left(\frac{\partial M}{\partial x}\right)_{\delta,t} = \left(\frac{\partial h}{\partial x}\right)_t \frac{M[A(1-M) - B\ell nM]}{h[A(1-h) - B\ell nh]} \tag{22}$$

where $h = h(x, t)$ is given by (16). Equation (22) is obtained by differentiating (15) with respect to x.

Substitution in (21) yields

$$t_x = \left(\frac{\partial \ell nh}{\partial x}\right)_t^{-1} [A(1-h) - B\ell nh]^{-1}$$

$$\times \int_{M[x_i(\delta)]}^{M[x_f(\delta)]} d\ell nM \{[A(1-M) - B\ell nM]R(M)\}^{-1} \tag{23}$$

$$= \left(\frac{\partial \ell nh}{\partial x}\right)_t^{-1} [A(1-h) - B\ell nh]^{-1} f(M_f, M_i) \tag{24}$$

where M_f and M_i are used to denote the two limits of integration in (23).

Image Profile Evaluation

The procedure for evaluating the developed image profile is summarized here. Results are described in the next section.

The aerial image intensity $I_0(x)$ incident on the CEF is determined by the projection optics. $I_c(1, x, t)$ is then obtained from (10) and (8). The lower limit of the integral in (15) is then calculated from the integral in (16). The development time, t_δ, required to clear the resist from the substrate in the regions where $I_c(1, x, t)$ has maxima, is obtained from (18) by setting the upper limit $\delta(x) = 1$. Equation (18) leads to the line profile at values of x, other than those corresponding to the maxima in $I_c(1, x, t)$. Therefore, the solution of equation (24) leads to the final image contour $x_f(\delta)$, once the model rate function R[M] has been specified.

Results

The developed image profile is obtained for the polysilane – AZ-2400 system of Hofer et al., [3], and the model CEL – positive resist combination of Mack [13] used by him to simulate CEM-388 type materials. In both cases, the incident light intensity is calculated using the projection optics subroutine from PROLITH. The results for the two resist systems are presented separately below.

Polysilane - AZ2400 Resist System

Since it is desired to compare the calculated profiles with experimentally determined profiles, the simulations here have been performed at the process conditions chosen by Hofer et al., in their experiments. For completeness, they are listed in Table 1. The development rate functions, R[M], employed in these calculations for the 5:1 and the 4:1 AZ2401 developers,

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are given explicitly by Hofer et al., (14). It should be noted that the exposure wavelength used by Hofer et al., is λ =313nm and that the image development using 5/1 water/AZ2401 developer requires a very long 660 seconds or more. The results are presented in several figures. Fig. 1. presents the normalized aerial image intensity distribution. Figure 2 shows the image profile as a function of development time in a 5:1 AZ2401 developer. The effect of surface inhibition on the profile is evident. The shape of the calculated profiles agrees very well with those reported by Hofer et al. For comparison, image profiles obtained in the absence of the polysilane film are shown, for otherwise fixed process conditions, in the same figure. Degradation of the image by a reduction in the side wall slope and resist thinning is obvious.

Since development with the 5:1 developer takes an unduly long time, the effect of using a 4:1 developer has been studied at two exposure doses, namely, 110mj/cm^2 and 180mj/cm^2. It may be noted from figure 3 that the 4:1 developer causes resist thinning at the lower exposure compared to the more dilute 5:1 developer, and the final image from an exposure at 180 mj/cm^2 and development with 5:1 solution is quite superior over all the other images.

CEM-388 Resist System

Finally, figure 4 shows the profiles obtained with the CEL-resist combination studied by Mack. The CEL used here is very similar to the CEM-388 manufactured by General Electric. The nominal parameters for the system are given in Table 2, containing the parameters for the development rate function R[M] proposed by Mack (13). Three CEL film thicknesses are investigated - 0.2, 0.4, and 0.6μm. Exposure energy for each thickness is

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adjusted to give the same nominal linewidth at the bottom of the opening after development for a fixed time of 60 seconds. No surface inhibition term is present in the dissolution rate function used here. The variation of the side wall angle with CEL thickness of the images in figure 4 is very close to that predicted by Mack from his PROLITH simulation study.

Conclusions

The concentration of the PAC in the underlying positive resist has been evaluated in a closed form, allowing for simultaneous bleaching of the contrast enhancing layer and the positive resist. Representing the resist development by a two stage process [10], [11] the resulting image profiles have been calculated for the polysilane-AZ2400 resist system studied by Hofer et al., and for a model CEM-388-resist combination investigated by Mack. Agreement with the experimental results of Hofer et al., and the calculations of Mack is very good.

Acknowledgements:

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References

[1] B.F. Griffing and P.R. West, 6th Intl. Conf. on Photopolymers, Ellenville, NY (1982).

[2] B.F. Griffing and P.R. West, Solid State Technol., 28 (5), 152 (1985).

[3] D.C. Hofer, R.D. Miller, C.G. Willson and A.R. Neureuther, Advances in Resist Technology I, Proc. SPIE, 469, 108 (1984).

[4] F.H. Dill, W.P. Hornberger, P.S. Hauge and J.M. Shaw, IEEE Trans. Elec. Dev., ED-22, 440 (1975).

[5] S.V. Babu and E. Barouch, IEEE Electron Dev. Lett., EDL-7, 252 (1986).

[6] S.V. Babu, IEEE Electron Dev. Lett. EDL-7, 250 (1986).

[7] S. V. Babu and E. Barouch, "Exposure-bleaching of nonlinear resist materials: Exact solution", IEEE Electron Dev. Letters (in press, September 1987).

[8] W.G. Oldham, IEEE Trans. Electron Dev. ED-34, 247–251, (1987).

[9] S.V. Babu and E. Barouch, "Exact Solution for the optical absorbtance of optical thin films", Studies in App. Math (in press).

[10] J.S. Greeneich, J. Appl. Phys., 45, 5264 (1974).

[11] M.P.C. Watts, J. Vac. Sci. and Tech. B3, 434 (1985).

[12] V. Srinivasan and S.V. Babu, Advances in Resist Technology and Processing III, Proc. SPIE, C.A. Willson (ed), 631 268–275, (1986).

14

[13] C. Mack, "Advanced topics in Lithography Modeling", in Advances in Resist Technology III, SPIE 631, 276–285, (1986), and J. Vac. Sci. and Tech., A (July/August 1987).

[14] D.C. Hofer, C.G. Willson, A.R. Neureuther, and M. Hakey, Proceedings SPIE, 334, 196 (1982).

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TABLE I

For polysilane simulations

Projection System:
$\lambda = 313$nm
$NA_o = 0.167$
$\sigma = 0.52$
defocus = 1.87μm
linewidth = 1.0μm
pattern = line-space pair

Resist Parameters: (AZ2400 @ 313nm)
A = $0.162/\mu$m
B = $0.184/\mu$m
C = 0.0128 cm^2/mJ
thickness = 1.25μm

CEL parameters (for 313nm)
$A_c = 8.93/\mu$m
$B_c = 0.175/\mu$m
$C_c = 0.0376$ cm^2/mJ
thickness = 0.2μm

Energy = 110mJ/cm^2 except where noted

TABLE II

For CEM simulations

Projection System:
  $\lambda = 405$nm
  $NA_o = 0.28$
  $\sigma = 0.70$
  no defocus
  linewidth = 0.8μm
  pattern = space (pitch = 4.0μm)

Resist parameters:
  $A = 0.6/\mu$m
  $B = 0.1/\mu$m
  $C = 0.020$ cm^2/mJ
  thickness = 0.8μm

CEL parameters:
  $A_c = 12.0/\mu$m
  $B_c = 0.10/\mu$m
  $C_c = 0.10$ cm^2/mJ

Developer conditions:
  Development time = 60 sec
  $R_{max} = 200$nm/sec
  $R_{min} = 1$nm/sec
  $M_{TH} = 0.5$
  $n = 5$

Exposure energy:
  variable (varied for a given CEL
  thickness so nominal linewidth
  attained in 60 sec development
  time.)

Figure Captions

Figure 1: Normalized aerial image intensity distribution of 1.00μm line-space pair $\lambda = 313$nm, $NA_o = 0.167$, $\sigma = 0.52$, and defocus $= 1.87\mu$m.

Figure 2: Simulated profiles of 1.00μm line-space pair in AZ2400 resist using 5:1 water/AZ2401 developer in the presence and in the absence of 0.2μm polysilane layer at various development times.

—— 575 sec - - - - 625 sec — — 675 sec —- —- 725 sec
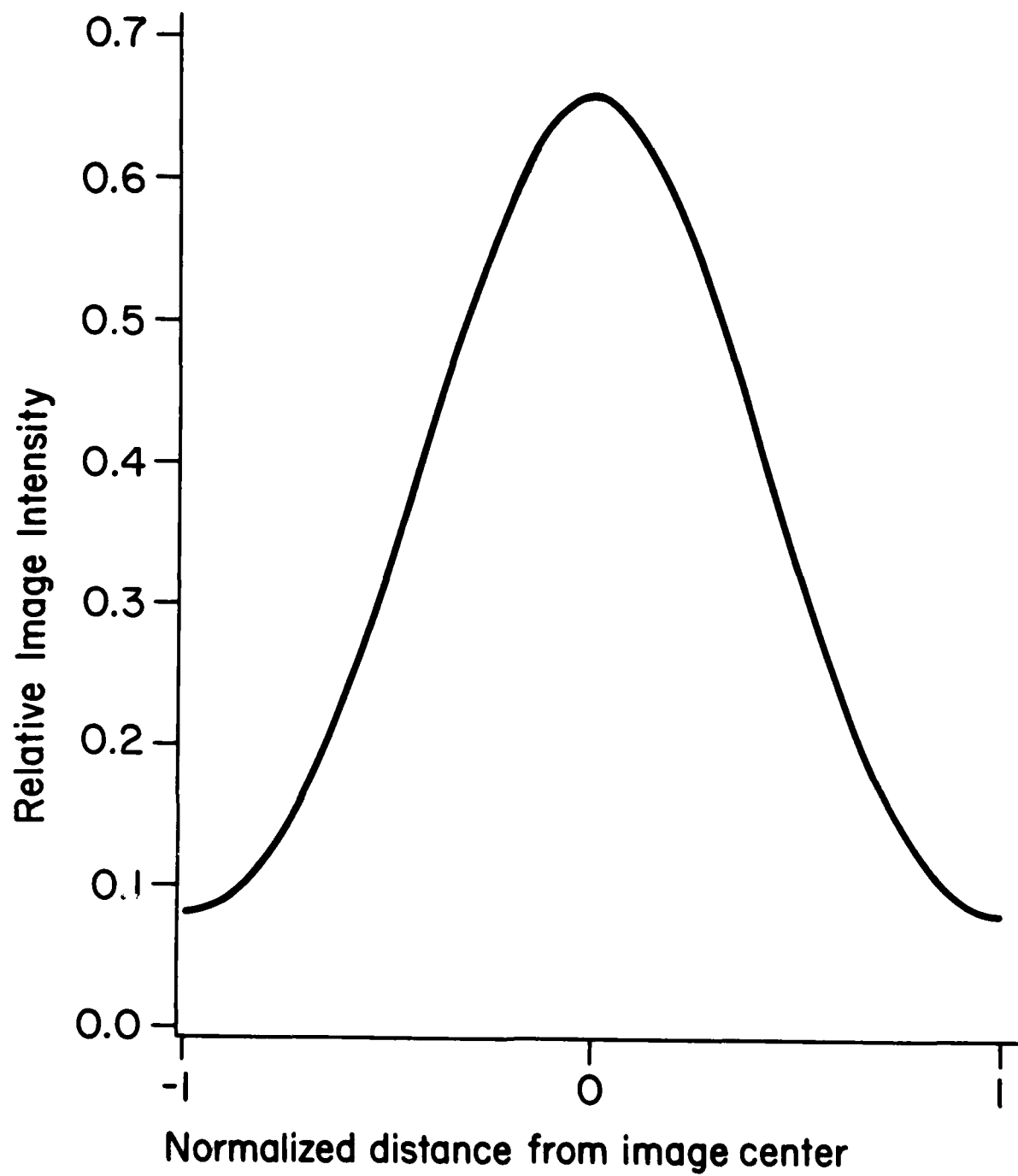
O w/polysilane layer   □ w/out polysilane layer

Figure 3: Simulated profiles of 1.00μm line-space pair in AZ2400 resist as a function of AZ2401 developer concentration and exposure energy.

———— 4:1 and 110mJ/cm^2 - - - 5:1 and 110mJ/cm^2
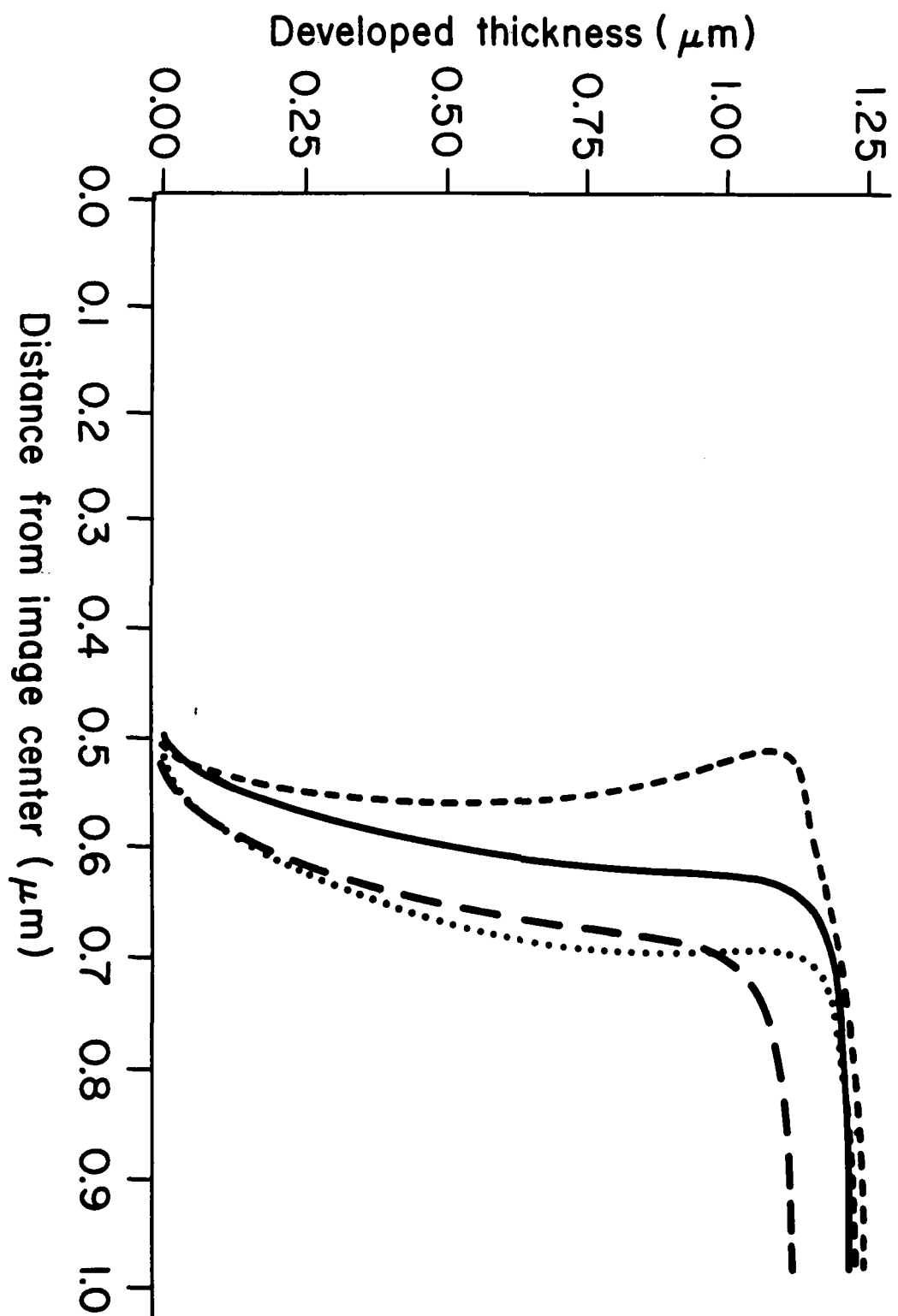
– – – 4:1 and 180mJ/cm^2 .... 5:1 and 180mJ/cm^2

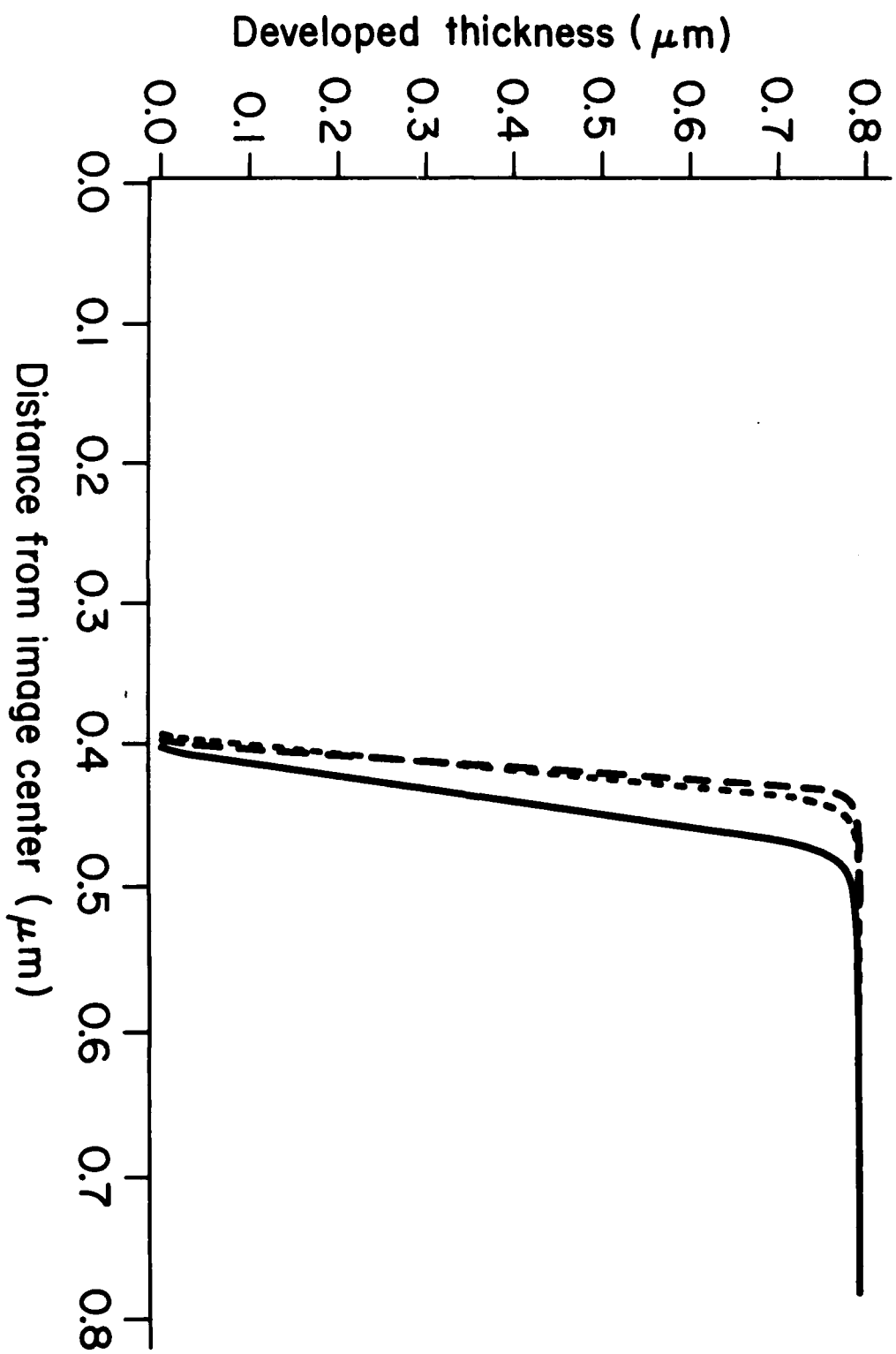Figure 4: Simulated profiles of 0.8μm isolated space in model CEM-positive resist system studied by Mack.

—— 0.2μm   – – – 0.4μm   — — — 0.6μm

  120.0mJ/cm^2 180.0mJ/cm^2 247.7mJ/cm^2

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3/280S-P4	12 SLOT SERVER			1.0	69930.00	69930.00
450A	ADD SECOND ETHERNET CNTRL			1.0	976.50	976.50
152A	FLOATING POINT ACCELERATOR			1.0	3430.00	3430.00
650B	60MB 1/4" TAPE SUBSYS			1.0	2800.00	2800.00
SYS3-02	SUN/OPSYS/68020,1/2",US DOCS			1.0	715.00	715.00
SYSL1	SUNOS RTU SINGLE USER			1.0	.00	.00
3/50M	3/50M CONFIGURABLE		2/05/87	1.0		
CONSISTING OF:						
3/50M-4-250	DESKTOP WRSTATION W/OCLI			1.0	5880.00	.00
152A	MC68881 FLOATING POINT COPROC			1.0	490.00	.00
SYSL1	SUNOS RTU SINGLE USER			1.0	.00	.00
SYS-09-3 X	SUN/OPSYS/REL3.X DOCS		2/05/87	4.0	175.000	700.00
3/260HM	3/260HM CONFIGURABLE		2/05/87	1.0	23730.00	23730.00
CONSISTING OF:						
3/260HM-8	12 SLOT HI-RES 8MB			1.0	23730.00	23730.00
SYSL1	SUNOS RTU SINGLE USER			1.0	.00	.00
W110-02	L/U 1/2" TP,RTU,DOCS,CA		2/05/87	1.0	6587.500	6587.50
SYS3-01	RTU,1/2",DOCS,SUNGKS ON 68020		2/05/87	1.0	.00	.00
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	881 FLOATING POINT COPROC			12.0		.00
	05 R10 SINGLE USER					
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